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IMPACT OF PHASE SEPARATION ON WASTE GLASS DURABILITY

Carol M. Jantzen, John B. Pickett, Kevin G. Brown , and Thomas B. Edwards
Westinghouse Savannah River Company
Aiken, SC 29808

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ABSTRACT

Phase separation is shown to have an adverse and unpredictable effect on durability of borosilicate nuclear waste glasses. The glass chemistry and thermal history of the waste glass during solidification in a canister can impact the kinetics of phase separation and thus, the long term durability of a the glass. Although waste glasses contain 15-20 components, many of the components are present in minor amounts. Greater than >95% of the glass chemistry is dominated by the seven major components, Na_2O- K_2O-Li_2O-SiO_2-Al_2O_3-B_2O_3-Fe_2O_3. Although the phase equilibria of this seven component system has never been studied, a compositionally dependent "Phase Separation Discriminator" was developed from a database of 88 High Level Waste (HLW) glasses shown experimentally to be homogeneous and 22 shown experimentally to be phase separated. This discriminator ensures that the HLW glasses produced in the Defense Waste Processing Facility (DWPF) are homogeneous and have predictable long term durability.

INTRODUCTION

High-level liquid nuclear waste (HLLW) at the Savannah River Site (SRS) is being immobilized by vitrification into borosilicate glass. The glass is produced and poured into stainless steel canisters in the Defense Waste Processing Facility (DWPF) for ultimate geologic disposal. The canistered borosilicate waste glass must comply with the Waste Acceptance Product Specifications (WAPS) established by the U.S. Department of Energy. WAPS Specification 1.3 relates to the ability of the vitrification process to consistently control the final waste form durability, i.e., the stability of the glass against attack by water.

The durability of the final DWPF glass is predicted by analysis of vitrified melter feed prior to transfer of the feed to the melter. The composition analysis is used to calculate a predicted durability for the DWPF production glass from the durability model, THERMO™ where the acrynoyn stands for Thermodynamic Hydration Energy Reaction MOdel [1]. In order to be fed to the melter, each batch of melter feed must produce a glass whose predicted durability response is more durable (by at least two standard deviations) than the benchmark waste glass identified in the DWPF Environmental Assessment (EA) based on ASTM C1285.

THERMO™ [1] is a first principles model that expresses the thermodynamic tendency of oxide species (components) in a glass to hydrate. THERMO™ only models the durability response of homogeneous glasses. Modeling of only homogeneous glasses avoids mixing different leaching mechanisms in one model. For example, homogeneous glasses undergo ion exchange and matrix dissolution while crystallized glasses undergo accelerated grain boundary dissolution and phase separated glasses undergo preferential soluble phase dissolution.. Crystallization and phase separation are normally detrimental to glass durability and are dependent on the volume fraction crystallized and/or the volume fraction phase separated. Since volume fraction is dependent on thermal history, and the thermal history of each canister is not identical, then mixed mechanism durability modeling of glass must be avoided.

Phase separated glasses are excluded in the THERMO™ process model based upon a compositionally derived phase separation discriminator. The basis for this additional product quality constraint, termed the homogeneity constraint, is described in this study.

BACKGROUND

Liquid-liquid phase separation is the growth of two or more non-crystalline glassy phases each of which will have a different composition from the overall melt [2]. Phase separation in glasses generally takes the form of immiscible liquid phases which differ in chemical composition, density, and surface tension. If the liquid-liquid immiscibility is “quenched in” when the glass is cooled to room temperature, it is often termed “glass-in-glass” phase separation.[1]

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[1] The two principle types of glass-in-glass phase separation are spinodal decomposition and homogeneous nucleation. Spinodal decomposition is small composition fluctuations (normally in the 20-500Å range) that cause the melt to separate into two phases spontaneously. The phase boundaries are diffuse and difficult to determine via electron microscopy. Homogeneous nucleation occurs when a critical size nucleus forms in the melt, it is not spontaneous in that a free energy barrier for the formation of the nucleus must be overcome. The phase boundaries are sharp and crystallization of the amorphous droplet phase often occurs [2].

Controlling the glass chemistry in compositional regions that avoid phase separation is key to controlling glass durability and processing. Factors such as the relative density of the two liquids, their viscosities, the interphase surface energy, and the melt conditions determine whether the two liquids separate on a gross macroscopic level resulting in two separate liquid layers in a melter or whether they may remain separated only on a microscopic scale [4].

Phase separation, if it occurs on a microscopic scale, has been shown to be detrimental to the stability and durability of nuclear waste glasses [1,5,6] because one of the immiscible phases is always more soluble than the other. Phase separation complicates modeling of glass durability as a function of composition, because the composition of the overall glass is known but the compositions of the two individual phases composing the glass is not known. If a glass is phase separated, the durability is dominated by the more soluble phase, causing the overall poorer durability of phase separated glasses (Figure 1).

Phase separation of the glass-in-glass type has been observed in multicomponent nuclear waste glasses (PNL77-107) containing >12 wt% B_2O_3 [7] , PNNL 76-68 containing 9.5 wt% B_2O_3 [4], and a Hanford waste glass formulated by PNNL with 13.3 wt% B_2O_3 [8]. Since waste glasses contain 15-20 components, phase separation in these complex systems is not well understood. However, many of the nuclear waste glass components are present in minor amounts and >95% of the glass chemistry is dominated by the seven major components, M_2O-SiO_2-Al_2O_3-B_2O_3-Fe_2O_3, where M = K + Na + Li.

Although the compositional dependency of phase separation in the individual M_2O-SiO_2-B_2O_3 systems [9] and in the (M_2O+MO)-(SiO_2+Al_2O_3)-B_2O_3 systems [9] where M_2O is any alkali oxide and MO is any alkaline earth oxide are known, phase separation in the M_2O-SiO_2-Al_2O_3-B_2O_3-Fe_2O_3 system has not previously been studied. Since both high level and low level waste

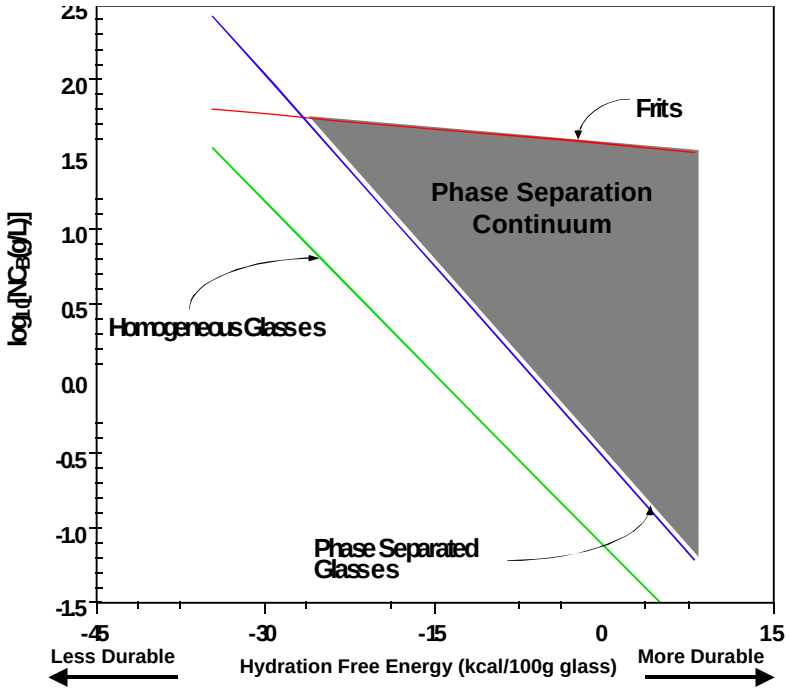


Figure 1.The first principles Thermodynamic Hydration Engery Reaction MOdel (THERMO™) distinguishes between the ASTM C1285 (PCT) response for phase separated glasses and homogeneous glasses. There appears to be a continuum of PCT response for phase separated glasses depending on the type and scale of the phase separation [1,10], e.g. phase separated waste glasses and phase separated frits give a different PCT response. In order to assure that the DWPF only processes homogeneous glasses, with predictable PCT responses, a phase separation discriminator or homogeneity constraint was developed and added to the Product Composition Control System (PCCS) [11] Statistical Process Control (SPC) system.

glasses contain Fe_2O_3 as a significant component , phase separation in the seven component system Na_2O-Li_2O-K_2O-SiO_2-Al_2O_3-B_2O_3-Fe_2O_3 is important to waste glass processing and glass durability.

MODELING AND EXPERIMENTAL APPROACH

A well analyzed and well characterized set of 110 glasses was used to determine the boundary of the glass-in-glass immiscibility boundary in the seven component Na_2O-Li_2O-K_2O-SiO_2-Al_2O_3-B_2O_3-Fe_2O_3 system. These homogeneous and phase separated glasses are designated as "Model Data" and are given by name and production mode in Table I. All glasses in “Model Data” met the following criteria: summed to 100±5 wt% oxide , were analyzed by Corning Engineering Laboratory Services (CELS) or bias corrected to CELS standards and contained 70-85wt% frit components.

An independent "Discriminator Validation Data" set was developed from glasses examined in this study and from the literature. The data was based on glass composition in oxide wt% and experimental observation of whether each glass was homogeneous or phase separated. Glasses in

the Discriminator Validation Data set often did not meet the stringent criteria that had been imposed on the “Model Data” set. The "Discriminator Validation Data" set does not contain any of the glasses from "Model Data" but does contain glasses that do not sum to 100±5 oxide wt%, contain greater than or less than 70-85 wt% frit components, and compositions that are as batched rather than as analyzed (as measured). The validation set of glasses is given in Table II. Table II indicates whether the individual glasses in the validation data set met the stringent criteria of “Model Data” or not. The “Validation Data Set” was used to validate the phase separation discriminator derived in this study.

The glasses in “Model Data” were fabricated under a variety of laboratory and pilot scale conditions by various researchers and vendors. Water quenching was used in the fabrication of many of the glass standards at Corning Engineering Laboratory Services (CELS). Water quenching is more rapid than air quenching, approximating quench rates of 5×10^4 to 1×10^5 °C/sec. Laboratory crucible melts were sometimes cooled by pouring the glass out of the crucible into a steel pan to represent the pouring of a small diameter melt stream in a pilot scale facility into a steel canister. Alternately, for small volume melts in ceramic and/or platinum crucibles the melts cooled rapidly enough in the crucibles that pouring was not necessary. All of these cooling histories are considered to be "air quenched" which yields a quench rate of 10^{-1} to 10^1 °C/sec depending on the thermal conductivity and size of the sample.

The glasses in “Model Data” were either analyzed by (1) Corning Engineering Laboratory Services (CELS) or (2) by the Analytic Development Section (ADS) or the Engineering Test Facility (ETF) laboratory of SRTC using standards traceable to CELS. The number of replicate analyses performed varied from 2 to 10 depending on whether the glass was an unknown (duplicates) or a standard (10 replicates).

X-ray Diffraction (XRD) analysis was performed on all of the Model data set and Validation data set glasses studied. Scanning Electron Microscopy (SEM) analyses coupled with Energy Dispersive Analysis by X-ray (EDAX) were performed on glasses to identify crystalline species below the detection limit of XRD and to identify large scale phase separation. The EA glass was examined by optical microscopy, SEM, and TEM in order to determine the crystallinity and/or homogeneity of the glass on a microscopic level. Additional glasses such as Pyrex, the Batch 1 study glasses, the white frit 202 glass which had been remelted and cooled on a steel block, and the Hanford glasses were analyzed by Transmission Electron Microscopy (TEM) for phase separation.

COMPOSITIONAL NATURE OF PHASE SEPARATION

In order to determine the compositional nature of the phase separation observed in the glasses in this study, it was necessary to examine the distribution of the oxide wt% concentrations of the homogeneous and phase separated glasses. Weight percent is used preferentially over normalized mole percents or mole fraction because glass-in-glass phase separation, including spinodal decomposition, is the separation of two immiscible phases that have different compositions and hence different densities [17-19]. Indeed, the dependence of the reciprocal of the density of each phase on the glass composition in weight percent is linear [17].

Table I.Glasses Comprising "Model Data" Set

Glasses By Classification	No. of Glasses	Analytical Laboratory
Homogeneous Glasses		
IDMS* Melter Hg Campaign	9	SRTC/ETF
AH Algorithm Glass Crucible Melts	29	CELS
DWPF Startup Frit, Fritted by Ferro	1	CELS
Waste Glass 202G and 202P Standards	2	CELS
Waste Glass 200R	1	SRTC/ADS
Waste Glass 165 CGW Standard	1	CELS
ARM-1 Approved Reference Glass	1	PNNL/MCC
Environmental Assessment Glass Standard	1	CELS
Waste Glass 131 TDS Crucible Melt	2	SRTC/ADS
Batch 1 Study 8,9,13,14,T Crucible Melt	5	SRTC/ADS
WCP Glass Standards		
Blend	1	CELS
Batch-1	1	CELS
Batch-2	1	CELS
Batch-3	1	CELS
Batch-4	1	CELS
HM	1	CELS
PX	1	CELS
IDMS* Melter Campaigns		
Blends-1	4	SRTC/ETF
Blends-2	5	SRTC/ETF
Blends-3	4	SRTC/ETF
IDMS* Melter Campaigns		
HM-1	4	SRTC/ETF
HM-2	3	SRTC/ETF
HM-3	3	SRTC/ETF
IDMS* Melter Campaigns		
PX-1	3	SRTC/ETF
PX-2	3	SRTC/ETF
Phase Separated Glasses		
IDMS* Melter Campaigns		
PX-4	3	SRTC/ETF
PX-5	9	SRTC/ETF
PX-6	1	SRTC/ETF
IDMS* Melter Campaigns PNNL Hanford (H) Glass	9	SRTC/ETF

Totals	**110**	**154**

Table II. Composition-Based Discriminator Validation Data

Sample ID	Type		Comment(s)
	Known	**Predicted**	
AH 168AL	ϕ Sep.[t]	ϕ Sep.	As Meas, Frit > 85%, SEM
PYREX	ϕ Sep.	ϕ Sep.	As Meas, Frit > 85%, Known f Sep.
NBS SRM 623	ϕ Sep.	ϕ Sep.	As Meas, Frit > 85%, TEM
MG-6	Homog.	Homog.	As Meas, TEM
MG-7	ϕ Sep.	ϕ Sep.	As Meas, Frit > 85%, TEM [12]
MG-9,18	Homog.	ϕ Sep.	As Meas, Frit > 85%, SEM [12]
MG-10,23,30	Homog.	Homog.	As Meas, Oxides(wt%) < 95%, SEM[12]
MG-17	Homog.	Homog.	As Meas, Oxides(wt%) > 105%, SEM [12]
MG-8,16,20,22,27 MG-29,32,33	Homog.	Homog.	As Meas, Frit < 70%, SEM [12]
Remaining 14 MG	Homog.	Homog.	As Meas, SEM [12]
FRIT 131,165	ϕ Sep.	ϕ Sep.	As Meas, Frit > 85%, SEM
FRIT 202	ϕ Sep.	ϕ Sep.	As Meas, Frit > 85%, SEM/TEM
CAC Glass 15,20	Homog.	Homog.	As Meas, TEM
CAC Glass 31	Homog.	Homog.	As Meas, Oxides(wt%) > 105%, TEM
Batch 1 Study 10,15	ϕ Sep.	ϕ Sep.	As Meas, Frit > 85%, TEM
PNL-77-268	ϕ Sep.	ϕ Sep.	As-Batched, Frit > 85%, TEM [7]
PNL-76-101	ϕ Sep.	ϕ Sep.	As-Batched, Frit > 85%, TEM [7]
PNL-77-269	ϕ Sep.	ϕ Sep.	As-Batched, TEM [7]
UK Glass M5 (189)	ϕ Sep.	ϕ Sep.	As-Batched, SANS [13]
PNL CVS-1-11	Homog.	Homog.	As-Batched/Meas., PNL SEM [5,14]
PNL CVS-2-30	Homog.	Homog.	As-Batched/Meas., PNL SEM [5,14]
PNL CVS-2-29	ϕ Sep.	ϕ Sep.	As-Batched/Meas., PNL SEM/TEM [5,14]
PNL CVS-2-31	ϕ Sep.	Homog.	As-Batched/Meas., PNL SEM/TEM [5,14]
Elmer Glass A,B	ϕ Sep.	ϕ Sep.	As-Batched, Frit > 85%, SEM [15]
Ventura Glass A,B	ϕ Sep.	ϕ Sep.	As-Batched, Frit > 85%, SEM [16]

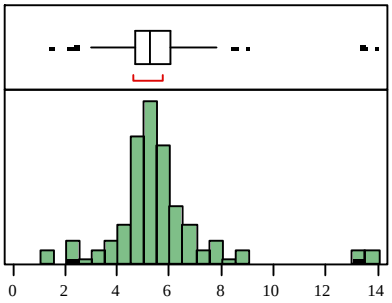
[t]" ϕ Sep." indicates phase separated glasses.

Graphical histograms were used to compare the differences in the compositional distributions between the 88 homogeneous and 22 phase separated glasses given in Table I. The histogram analysis of the glass chemistry in oxide wt% indicated that the phase separated glasses were significantly lower in Al_2O_3 while being somewhat higher in B_2O_3 (Figure 2). The homogeneous glasses had about the same concentrations of Na_2O, Li_2O, SiO_2, and K_2O as the

phase separated glasses (Figure 1). Significant differences in the concentrations of other glass oxide components, e.g., CaO and FeO were not observed.

Visualization of the immiscibility region in the seven component Na_2O-Li_2O-K_2O-SiO_2-Al_2O_3-B_2O_3-Fe_2O_3 system is difficult. In order to simplify the graphical representation Na_2O,Li_2O, and K_2O can be represented as one corner in the pseudoquaternary system. M_2O-(SiO_2+Al_2O_3)-B_2O_3-Fe_2O_3 system. However, in this pseudoquaternary representation the high SiO_2 and Al_2O_3

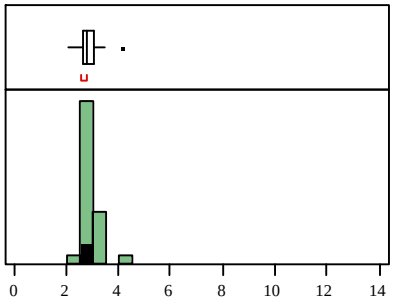
Homogeneous Al_2O_3 (wt%)



Quantiles		
maximum	100.0%	13.900
	99.5%	13.900
	97.5%	13.478
	90.0%	7.676
quartile	75.0%	6.040
median	50.0%	5.255
quartile	25.0%	4.700
	10.0%	3.582
	2.5%	1.566
	0.5%	1.360
minimum	0.0%	1.360

Moments	
Mean	5.65514
Std Dev	2.21459
Std Err Mean	0.23608
upper 95% Mean	6.12437
lower 95% Mean	5.18591
N	88.00000
Sum Wgts	88.00000

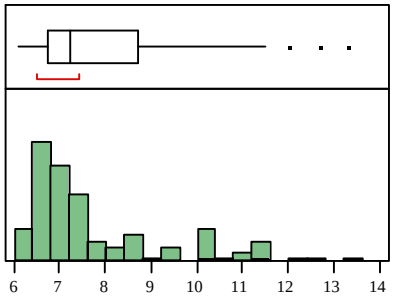
Phase Separated Al_2O_3 (wt%)



Quantiles		
maximum	100.0%	4.1700
	99.5%	4.1700
	97.5%	4.1700
	90.0%	3.4220
quartile	75.0%	3.0725
median	50.0%	2.8100
quartile	25.0%	2.6200
	10.0%	2.5630
	2.5%	2.0700
	0.5%	2.0700
minimum	0.0%	2.0700

Moments	
Mean	2.89591
Std Dev	0.41531
Std Err Mean	0.08854
upper 95% Mean	3.08005
lower 95% Mean	2.71177
N	22.00000
Sum Wgts	22.00000

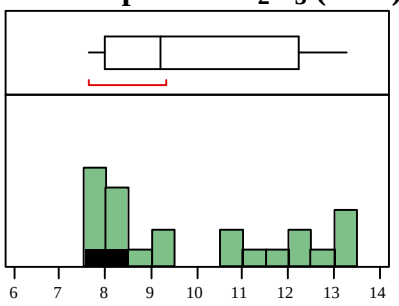
Homogeneous B_2O_3 (wt%)



Quantiles		
maximum	100.0%	13.300
	99.5%	13.300
	97.5%	12.542
	90.0%	10.800
quartile	75.0%	8.713
median	50.0%	7.225
quartile	25.0%	6.760
	10.0%	6.484
	2.5%	6.134
	0.5%	6.100
minimum	0.0%	6.100

Moments	
Mean	7.91432
Std Dev	1.70627
Std Err Mean	0.18189
upper 95% Mean	8.27584
lower 95% Mean	7.55279
N	88.00000
Sum Wgts	88.00000

Phase Separated B_2O_3 (wt%)



Quantiles		
maximum	100.0%	13.280
	99.5%	13.280
	97.5%	13.280
	90.0%	13.110
quartile	75.0%	12.237
median	50.0%	9.210
quartile	25.0%	7.980
	10.0%	7.670
	2.5%	7.620
	0.5%	7.620
minimum	0.0%	7.620

Moments	
Mean	9.97227
Std Dev	2.14729
Std Err Mean	0.45780
upper 95% Mean	10.92432
lower 95% Mean	9.02023
N	22.00000
Sum Wgts	22.00000

Figure 2. Histogram analysis of the compositional differences (in wt%) of phase separated and homogeneous glasses.

content of all these glasses cluster at the (SiO_2+Al_2O_3) apex . Alternatively, the SiO_2 content of the 110 glasses was assumed to be approximately constant (varying only from 40 to 65 wt%) and the remaining elements renormalized and plotted in the pseudoquaternary system $\sum M_2O$-Fe_2O_3-Al_2O_3-B_2O_3 composition space (Figure 3). The shaded region in Figure 3 sharply delineates a compositional difference in weight percent composition space between the phase separated glasses and the homogeneous glasses: sharp phase boundaries in weight percent composition space are indicative of immiscibility boundaries.

Figure 2 indicates that the phase separated glasses are highly dependent on the Al_2O_3 content of the glass. This is in agreement with the strong difference in the Al_2O_3 concentration of the phase separated glasses and the homogeneous glasses noted in the oxide component distribution analysis (Figure 2). This is also in agreement with the widely known effects of increased Al_2O_3 to stabilize glasses against phase separation [9]. It is also in agreement with the natural basalt analog quaternary system Na_2O-Al_2O_3-Fe_2O_3-SiO_2 shown in Figure 4 which depicts a region of immicibility in alkali iron silicates with less than ~ 4 wt% Al_2O_3 [20].

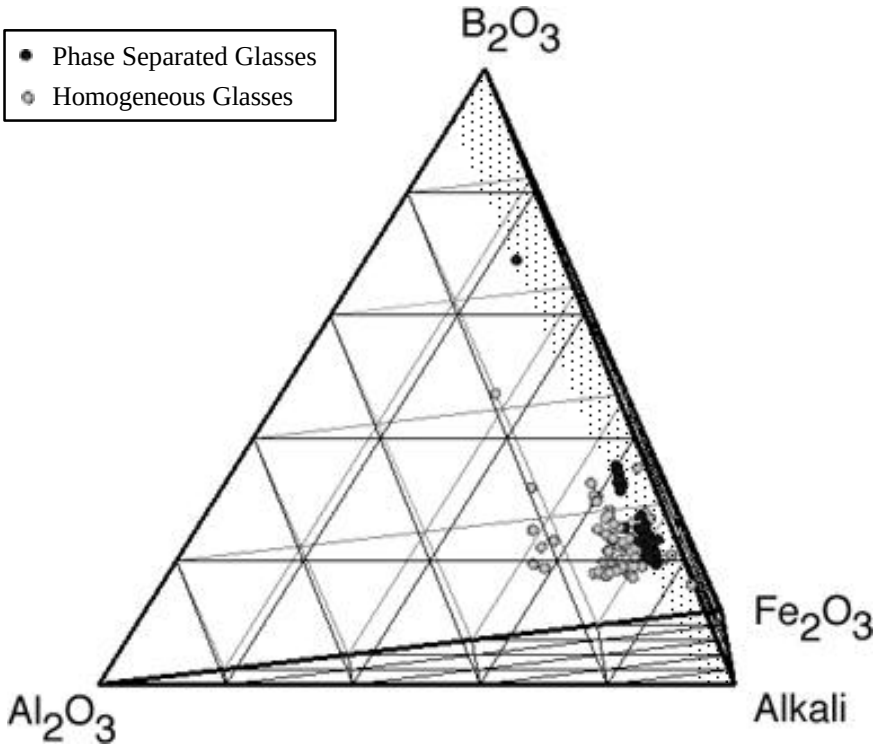


Figure 3.The homogeneous and phase separated glasses examined in this study plotted in Al_2O_3-B_2O_3-$\sum M_2O$-Fe_2O_3 composition space indicate that the phase separated glasses (shaded region) are low in Al_2O_3 content relative to the homogeneous glasses.

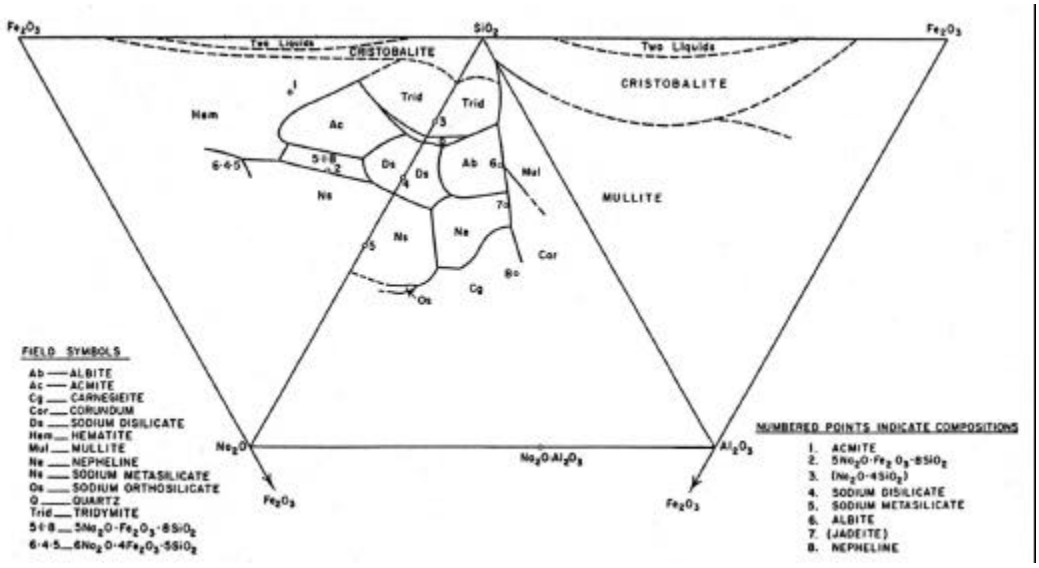


Figure 4. The quaternary system Na_2O-Al_2O_3-Fe_2O_3-SiO_2 of geologic significance which shows the phase relations in this complex system. The three faces of the tetrahedron are shown laying flat in the plane of the base of the system (from reference 20) and there is a region of liquid-liquid immiscibility shown in the Fe_2O_3-Al_2O_3-SiO_2 subsystem and the Fe_2O_3-SiO_2-Na_2O subsystem below ~ 4 wt% Al_2O_3.

DEVELOPMENT OF THE PHASE SEPARATION DISCRIMINATOR

Based on the oxide distribution analysis and the visualization of the homogeneous and inhomogeneous glass chemistry in the ternary $\sum M_2O$-(SiO_2+Al_2O_3)-B_2O_3) [1] and quaternary $\sum M_2O$-Al_2O_3-B_2O_3-Fe_2O_3) composition spaces (Figure 3) a compositional relationship for the phase separated vs. the homogeneous glasses was determined based primarily on the seven major components which dominate $\geq$95% of the glass chemistry, e.g., Na_2O-Li_2O-K_2O-Al_2O_3-B_2O_3-Fe_2O_3-SiO_2.

Good discrimination between the homogeneous and phase separated glasses was achieved by plotting the sum of the lighter density alkali borosilicate (primarily frit) components vs. the heavier density sludge components, e.g. Al_2O_3 plus all of the iron present as Fe_2O_3. Calcium oxide, MoO_3, and the rare earths (i.e., Nd_2O_3, Ce_2O_3, La_2O_3, and Y_2O_3) were included as heavier density componoents to properly account for the sludge components.† Since the

† In this study, the MoO_3 and rare earth oxides only occurred in the Hanford glasses including the ARM-1 reference glass although these species are also anticipated in DWPF glasses. Calcium oxide was included since it was present in most of the glasses,

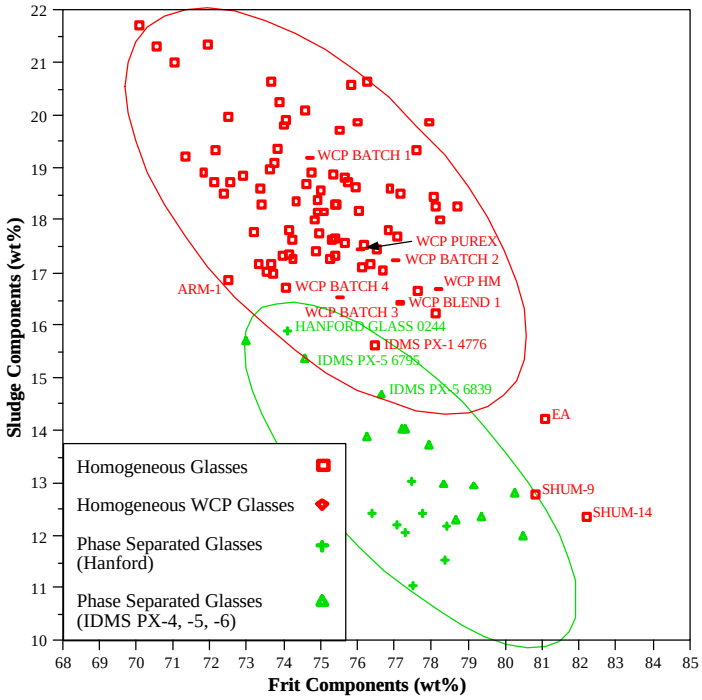
compositions of the glasses in this study were not statistically designed, certain minor sludge components (e.g., NiO, MnO, MgO, SrO, and ZrO_2) were found to be insignificant to the discrimination and were thus omitted from the definition of the heavier density component.††

The discriminant analysis was generated in 14 dimensional (14 component) oxide wt% space. Figure 5 shows this representation in 2 dimensional space as overlapping ellipses. The discriminate function distinguishes between homogeneous and phase separated glasses on a compositional basis. Glasses will be homogeneous if the following criterion is satisfied:

$$-1.6035\ x - 5.6478\ y + 210.9203 < 0 \quad (1)$$

where y = Denser Components = Al_2O_3 + (Fe_2O_3 + FeO calculated as Fe_2O_3) + Nd_2O_3 + Ce_2O_3 + La_2O_3 + Y_2O_3 + CaO + MoO_3 (wt%)

x = Less Dense Components = Na_2O + Li_2O + K_2O + Cs_2O + SiO_2 + B_2O_3 (wt%)



including significant amounts in ARM-1, 200R, and the CGW 165 STD. Furthermore, CaO was included because it can play a role in phase separation in borosilicate glasses[9].

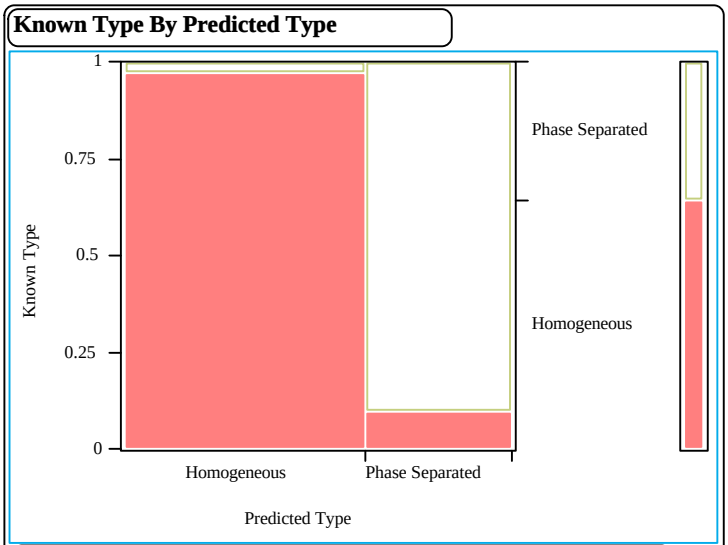
†† Many of these elements are highly correlated to the major sludge oxides, e.g., Al_2O_3 and Fe_2O_3, and their inclusion tends to include considerable noise into the discrimination with minimal improvement.

Figure 5.Compositional distinction between homogeneous and phase separated glasses. 95% confidence ellipsoids are indicated for both the homogeneous and phase separated glasses.

Analysis of the distribution of the lighter components between the homogeneous and phase separated glasses in Table I indicates that the homogeneous glasses contain lower amounts of frit components than the phase separated glasses. The phase separated glasses are stabilized by a higher concentration of frit components (77.5 ± 3.6 wt%) than homogeneous glasses (75.2 ± 4.4 wt%).

STATISTICAL VALIDATION OF THE PHASE SEPARATION DISCRIMINATOR

The results of the validation for the composition-based discriminant function represented by Equation 1 are summarized in Figure 6. Of the 53 validation glasses described in Table II, 34 were found homogeneous and 19 phase separated by either SEM, TEM, and/or SANS. Of the 34 known homogeneous glasses, 32 (or 94%) were correctly classified by Equation 1. Of the 19 known phase separated glasses, 18 (or 95%) were correctly classified. Note this is the more dangerous type of error as during production it is more conservative to err on the side of predicting a glass to be phase separated when it is not rather than vice versa. Thus approximately 95% of the glasses in Table II were discriminated appropriately despite the fact that only a few satisfied all the stringent “Model Data” criteria under which the discriminator was developed .



Crosstabs

Known Type \ Predicted Type	Homogeneous	Phase Separated	
Count			
Homogeneous	32	2	34
Phase Separated	1	18	19
	33	20	53

Figure 6. Results of the Phase Separation Composition Discriminator for DWPF and non-DWPF data.

DISCUSSION

The need for a compositional phase separation discriminator to be used in conjunction with a glass durability model such as THERMO™ is apparent in the studies of Tovena, et al [6] who demonstrated that the Jantzen/Plodinec free energy model [21] as well as the Feng/Barkatt enthalpy model [22-23] and the Bray/Yun [24-25] structural durability models did not predict waste glass durability accurately when the glasses contained >15% B_2O_3 with little or no Al_2O_3. For these glasses all the previous models underpredicted the glass durability significantly. These authors [6] attributed the underprediction to phase separation and complete dissolution of the borate phase in the absence of alumina in the glass.

Glass durability cannot be predicted from composition unless the compositional regions of glass-in-glass phase separation are clearly delineated and avoided during waste glass processing. This was implemented by the DWPF prior to non-radioactive startup in 1994 by the addition of the phase separation discriminator (known as the homogeneity constraint) into the statistical process control system, PCCS, that is used to simultaneously produce durable and processable glass. This is illustrated graphically in Figure 7 where the durability, viscosity, liquidus and homogeneity constraints define the durable and processable DWPF waste glass compositions.

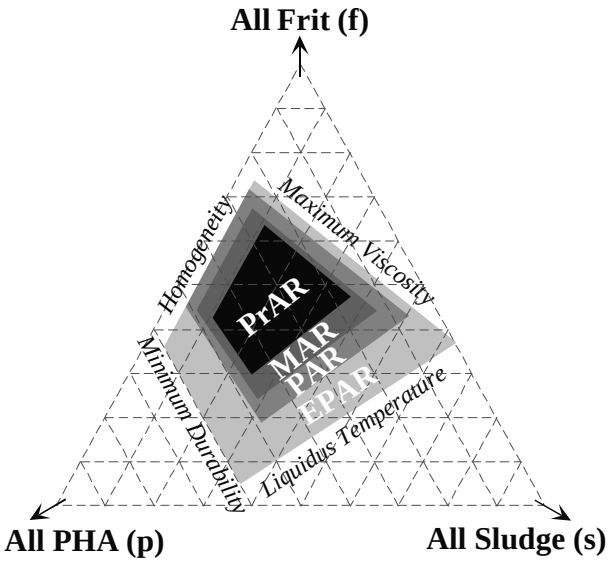


Figure 7. Schematic of the multiple constraints, including a glass homogeneity constraint, applied to the DWPF process to ensure with $\geq$95% confidence that homogeneous durable and processable glasses are produced.

CONCLUSIONS

A region of liquid-liquid immiscibility is defined in a 14 component waste glass systm in term of a compositionally dependen phase separation discriminator . The discriminator function is defined in wt% and the two phases separating represent different melt densities. Glasses will be homogeneous if the following criterion is satisfied:

$$-1.6035\ x - 5.6478\ y + 210.9203 < 0 \quad (1)$$

where y = Denser Components = Al_2O_3 + (Fe_2O_3 + FeO calculated as Fe_2O_3) + Nd_2O_3 + Ce_2O_3 + La_2O_3 + Y_2O_3 + CaO + MoO_3 (wt%)

x = Less Dense Components = Na_2O + Li_2O + K_2O + Cs_2O + SiO_2 + B_2O_3 (wt%)

This constraint, when used to screen phase separated glasses out of a statistically designed study or out of a glass durability database, ensures that only homogeneous waste glass durability is being modeled. This also prevents mixed mechanism durability modeling which would otherwise allow phase separated waste glasses to be produced and durability to be incorrectly underpredicted.

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